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[Filed Document Name]	Abstract	1
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An Ink Composition for Ink Jet Printer

[Claims]

[Claim 1] An aqueous ink composition comprising at least water, a pigment dispersed by polymer, a sulfonyl group-containing (co)polymer, and an ultra-penetrating agent.

[Claim 2] The aqueous ink composition according to claim 1, wherein the sulfonyl group-containing (co)polymer is incorporated in the form of an emulsion of the sulfonyl group-containing (co)polymer.

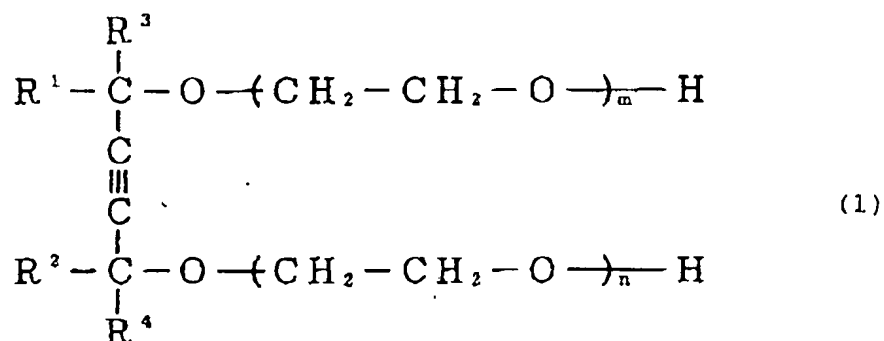
[Claim 3] The aqueous ink composition according to claim 1 or 2, wherein the sulfonyl group-containing (co)polymer is a diene-based sulfonyl group-containing (co)polymer and/or a non-diene-based sulfonyl group-containing (co)polymer.

[Claim 4] The aqueous ink composition according to claim 3, wherein the non-diene-based sulfonyl group-containing (co)polymer is an acrylic sulfonyl group-containing (co)polymer.

[Claim 5] The aqueous ink composition according to claim 1, wherein the ultra-penetrating agent is at least one of acetylene glycol compounds, acetylene alcohol compounds, and glycol ether compounds.

[Claim 6] The aqueous ink composition according to claim 1, wherein the ultra-penetrating agent is a compound represented by the following formula 1 and triethylene glycol monobutyl ether.

[Ka 1]



(wherein,  $0 \leq m+n \leq 50$ , and  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  each independently is an alkyl group)

[Claim 7] The aqueous ink composition according to any one of claims 1 to 6, which is an ink composition for ink jet recording.

[Claim 8] A recording method wherein recording is conducted by an ink jet recording method using the aqueous ink composition according to any one of claims 1 to 6.

[Claim 9] An ink cartridge containing the aqueous ink composition according to any one of claims 1 to 6.

[Claim 10] Recorded matter recorded by the recording method according to claim 8.

[Detailed Description of the Invention]

{0001}

[Technical Field to which the Invention Belongs]

The present invention relates to an aqueous ink composition which, without impairing ejection stability, is excellent in light-fastness and water-fastness, does not cause cohesion differential, gloss differential, bronzing phenomenon, color-bleeding, and the like, and has improved fixing ability and coloring property, in particular, an aqueous ink composition suitable for ink jet printing, a recording method using the aqueous ink composition, recorded matter recorded by the recording method, and an ink cartridge containing the aqueous ink composition.

[0002]

[Prior Art]

An aqueous ink composition generally contains water as a main component, to which a coloring component and a wetting agent such as glycerin are incorporated. Moreover, recording media to be used for the aqueous ink composition include those capable of absorbing the ink composition to some extent and of being penetrated by a colorant, for example, paper. As a recording method using an aqueous ink composition, an ink jet recording method has recently attracted an attention. Ink jet recording method is a recording method wherein droplets of an ink composition are ejected through fine nozzles

and deposited onto a recording medium to conduct recording.

[0003]

Hitherto, a water-soluble dye has been frequently employed as a colorant for an aqueous ink composition to be used in ink jet printing method, so that there exists a defect that the light-fastness and water-fastness of recorded matter are poor. On the other hand, it has been examined to employ a pigment as a colorant for improving the light-fastness and water-fastness of recorded matter, but there arises a problem that fixing ability onto a recording medium is insufficient in the case of employing a pigment as a colorant.

[0004]

In addition, color-bleeding may occur depending on recording media owing to the slow penetration of an ink composition, and therefore, it is examined to incorporate an acetylene glycol-type or glycol ether-type penetrating agent. However, even in the case of an ink composition wherein the penetrating ability of the ink is enhanced by the use of the penetrating agent, the penetrating ability is still insufficient depending on recording media and thus, there sometimes occurs a phenomenon that color density becomes uneven (hereinafter, referred to as "cohesion differential"). Accordingly, the present

inventors have found a problem that ejecting amount of the ink composition cannot be increased and thus coloring property cannot be improved, especially in the case that recording is conducted by overlapping two or more colors.

[0005]

Furthermore, in the case of conventional ink compositions, the inventors have found problems of occurrence of a phenomenon that difference in reflectance is observed depending on print duties (hereinafter, referred to as "gloss differential") and occurrence of a phenomenon that a solid print of cyan looks reddish (hereinafter, referred to as "bronzing").

[0006]

[Problems that the Invention is to Solve]

The invention is conducted in consideration of the above problems, and objects thereof are to provide an aqueous ink composition excellent in light-fastness and water-fastness, which is excellent in light-fastness and water-fastness does not cause cohesion differential, gloss differential, bronzing, color-bleeding, and the like without impairing ejection stability, and has improved fixing ability and coloring property, and also to provide a recording method using the aqueous ink composition, recorded matter recorded by the recording



method, and an ink cartridge containing the aqueous ink composition.

[0007]

[Means for Solving the problems]

The aqueous ink composition of the invention comprising at least water, a pigment dispersed by polymer, a sulfonyl group-containing (co)polymer, and an ultra-penetrating agent, whereby the above object is achieved.

[0008]

Moreover, the aqueous ink composition of the invention is the composition wherein the sulfonyl group-containing (co)polymer is mixed as an emulsion of the sulfonyl group-containing (co)polymer.

[0009]

The aqueous ink composition of the invention is the composition wherein the sulfonyl group-containing (co)polymer is a diene-based sulfonyl group-containing (co)polymer and/or a non-diene-based sulfonyl group-containing (co)polymer.

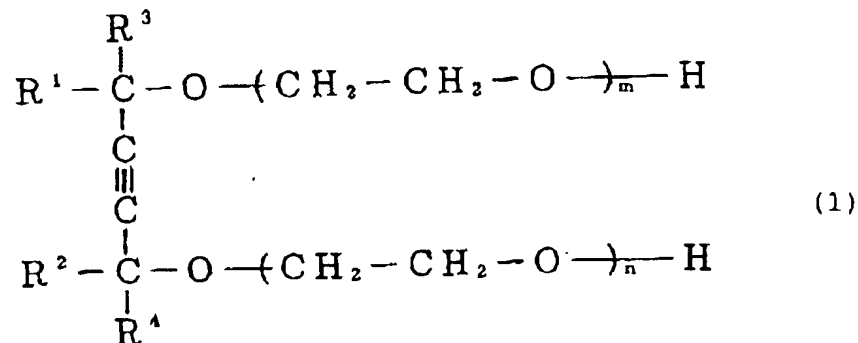
[0010]

The aqueous ink composition of the invention is the composition wherein the ultra-penetrating agent is at least one of acetylene glycol compounds, acetylene alcohol compounds, and glycol ether compounds.

[0011]

The aqueous ink composition of the invention is the composition wherein the ultra-penetrating agent is a compound represented by the following formula 1 and triethylene glycol monobutyl ether.

[Ka 2]



(wherein,  $0 \leq m+n \leq 50$ , and  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$  each independently is an alkyl group)

[0012]

The aqueous ink composition of the invention is the composition which is an aqueous ink composition for ink jet recording.

[0013]

A recording method wherein recording is conducted by an ink jet recording method using the aqueous ink composition described in any one of the above.

[0014]

An ink cartridge containing the aqueous ink composition described in any one of the above.

[0015]

Recorded matter produced by an ink jet recording method using the aqueous ink composition described in any one of the above.

[0016]

[Mode for Carrying Out the Invention]

The following will explain the aqueous ink composition of the invention in detail.

The aqueous ink composition of the invention is obtainable by mixing at least water, a "pigment dispersed by polymer", a "sulfonyl group-containing (co)polymer", and an "ultra-penetrating agent".

In the invention, the "aqueous ink composition" means an aqueous black ink composition for monochromatic recording, and an aqueous color ink composition, specifically an aqueous cyan ink composition, an aqueous magenta ink composition, or an aqueous yellow ink composition, or also in some cases, an aqueous black ink composition, for color recording.

In the invention, the "pigment dispersed by polymer" means a pigment which is dispersed and/or dissolved in an aqueous medium (water or a mixture of water and a water-soluble organic solvent) by the action of a polymeric dispersant (described later) or a polymeric dispersant and other dispersant.

In the invention, the "sulfonyl group-containing (co)polymer" means a sulfonyl group-containing polymer (described later) and/or a sulfonyl group-containing copolymer (described later).

[0017]

As the pigment to be contained in the aqueous ink composition of the invention, there may be employed an inorganic pigment and an organic pigment which has hitherto been employed in ink composition for ink jet recording. Examples of the inorganic pigment usable include carbon blacks produced by known methods such as contact process, furnace process, and thermal process, in addition to titanium oxide and iron oxide. Moreover, examples of the organic pigment usable include azo pigments (including azo lakes, insoluble azo pigments, condensed azo pigments, chelate azo pigments, for example), polycyclic pigments (for example, phthalocyanine pigments, perylene pigments, perinone pigments, anthraquinone pigments, quinacridone pigments, dioxazine pigments, thioindigo pigments, isoindolinone pigments, and quinophthalone pigments), nitro pigments, nitroso pigments, and aniline black.

[0018]

The colorant for the cyan ink composition is preferably a cyan pigment.

As the cyan pigment, C. I. Pigment Blue 15:3, 15:4, 60, and the like are preferably employed, and particularly preferred is C. I. Pigment Blue 15:3.

Moreover, the colorant for the magenta ink composition is preferably a magenta pigment.

As the magenta pigments, C. I. Pigment Red 122, 202, 209, C. I. Pigment Violet 19, and the like are preferably employed, and particularly preferred is C. I. Pigment Red 122.

These cyan pigments and magenta pigments may be used solely or as a mixture of two or more.

[0019]

Moreover, a yellow pigment and a black pigment are preferably used as colorants for the yellow ink composition and black ink composition, respectively.

The yellow pigment includes C. I. Pigment Yellow 74, 93, 109, 110, 128, 138, 150, 151, 154, 155, 180, 185, and the like, and the black pigment includes carbon black and the like.

[0020]

Furthermore, as pigments to be used for color ink compositions other than cyan, magenta, or yellow ink composition, e.g., orange ink composition and green ink composition, there may be mentioned C. I. Pigment Orange

36, 43, or the like and C. I. Pigment Green 7, 36, or the like.

[0021]

The particle diameter of the pigment to be contained in the aqueous ink composition is preferably 10  $\mu\text{m}$  or less, more preferably 0.1  $\mu\text{m}$  or less.

Moreover, the content of the pigment in the aqueous ink composition is not particularly limited but is preferably from 0.1 to 20% by weight, more preferably from 0.2 to 10% by weight.

[0022]

The pigment is used as a dispersion in an aqueous medium (water or a mixture of water and a water-soluble organic solvent) dispersed by the action of a polymeric dispersant or a polymeric dispersant and other dispersant, i.e., as a "pigment dispersed by polymer".

[0023]

As a preferable example of the polymeric dispersant, a natural polymer may be mentioned. Specific examples thereof include proteins such as glue, gelatin, and albumin; natural rubbers such as gum arabic and gum tragacanth; glycosides such as saponin; alginic acid and alginic acid derivatives such as alginate ester of propylene glycol, triethanolamine alginate, and ammonium alginate; cellulose derivatives such as methyl cellulose,

carboxymethyl cellulose, hydroxyethyl cellulose, and ethyl hydroxycellulose; and the like.

[0024]

A synthetic polymer may be also mentioned as a preferable example of the polymeric dispersant. Specific examples thereof include polyvinyl alcohols; polyvinyl pyrrolidones; acrylic resins such as polyacrylic acid, acrylic acid-acrylonitrile copolymer, potassium acrylate-acrylonitrile copolymer, vinyl acetate-acrylic ester copolymers, and acrylic acid-alkyl acrylate copolymers; styrene-acrylic resins such as styrene-acrylic acid copolymer, styrene-methacrylic acid copolymer, styrene-methacrylic acid-alkyl acrylate copolymers, styrene- $\alpha$ -methylstyrene-acrylic acid copolymer, and styrene- $\alpha$ -methylstyrene-acrylic acid-alkyl acrylate copolymers; styrene-maleic acid copolymer; styrene-maleic anhydride copolymer; vinyl naphthalene-acrylic acid copolymer; vinyl naphthalene-maleic acid copolymer; vinyl acetate copolymers such as vinyl acetate-ethylene copolymer, vinyl acetate-fatty acid vinyl ethylene copolymer, vinyl acetate-maleic ester copolymer, vinyl acetate-crotonic acid copolymer, and vinyl acetate-acrylic acid copolymer; and salts thereof.

Among them, particularly preferred is a copolymer obtainable from a monomer having a hydrophobic group and

a monomer having a hydrophilic group or a polymer obtainable from a monomer having both of a hydrophobic group and a hydrophilic group in the molecular structure. Examples of the above salts include salts with diethylamine, ammonia, ethylamine, triethylamine, propylamine, isopropylamine, dipropylamine, butylamine, isobutylamine, triethanolamine, diethanolamine, aminomethylpropanol, and morpholine. These copolymers have a weight average molecular weight of preferably 3000 to 30000, more preferably 5000 to 15000.

[0025]

As other dispersant which can be used in combination at the preparation of the pigment dispersed by polymer, a conventional water-soluble ionic or nonionic surfactant may be mentioned.

Examples of anionic surfactants include higher fatty acid salts, higher alkyl dicarboxylate salts, higher alcohol sulfate ester salts, higher alkylsulfonate salts, condensates of higher fatty acids and amino acids, sulfosuccinate ester salts, naphthenate salts, liquid fatty oil sulfate ester salts, alkylarylsulfonate salts, and the like.

Examples of cationic surfactants include aliphatic amine salts, quaternary ammonium salts, sulfonium salts,



and phosphonium salts, and examples of amphoteric surfactants include polyacrylamide.

Examples of nonionic surfactants include fatty acid esters of polyoxy compounds, and polyethylene oxide condensates.

[0026]

One or more of these dispersants may be used.

Moreover, the adding amount of these dispersants is preferably in the range of 0.06 to 3% by weight, more preferably in the range of 0.125 to 3% by weight relative to the pigment 1.

[0027]

The pigment dispersed by polymer to be used in the invention can be prepared by stirring and mixing, for example, a pigment, a polymeric dispersant or a polymeric dispersant and other dispersant, and an aqueous medium by means of, for example, beads mill, ball mill, sand mill, attriter, roll mill, agitator, Henschell mixer, colloid mill, ultrasonic homogenizer, or pearl mill.

[0028]

The sulfonyl group-containing (co)polymer to be contained in the aqueous ink composition of the invention is obtained by sulfonating a polymer or copolymer obtainable by polymerization or copolymerization of the following monomer(s) (refer to Japanese Patent Laid-Open

No. 217525/1999), or is obtained by polymerizing or copolymerizing sulfonated monomer(s), and includes a diene-based sulfonyl group-containing (co)polymer which requires a diene-based monomer as the essential component and a non-diene-based sulfonyl group-containing (co)polymer which does not requires a diene-based monomer as the essential component.

In the aqueous ink composition of the invention, the sulfonyl group-containing (co)polymer is preferably used as an emulsion. The use of the composition containing an emulsion of a sulfonyl group-containing (co)polymer enables the improvement of fixing ability without impairing ejection stability, and also enables the suppression of occurrence of cohesion differential, gloss differential, and bronzing and the increase of print duty which may be resulted from the combined use of an ultra-penetrating agent, whereby the enhancement of coloring property is enabled.

[0029]

The monomers employed for obtaining the diene-based sulfonyl group-containing (co)polymer include diene-based monomers and other monomers usable in combination with the diene-based monomers.

The diene-based monomers are diene-based compounds having 4 to 10 carbon atoms, and examples thereof include

1,3-butadiene, 1,2-butadiene, 1,3-pentadiene, 1,2-pentadiene, 2,3-pentadiene, isoprene, 1,2-hexadiene, 1,3-hexadiene, 1,4-hexadiene, 1,5-hexadiene, 2,3-hexadiene, 2,4-hexadiene, 2,3-dimethyl-1,3-butadiene, 2-ethyl-1,3-butadiene, 1,2-heptadiene, 1,3-heptadiene, 1,4-heptadiene, 1,5-heptadiene, 1,6-heptadiene, 2,3-heptadiene, 2,5-heptadiene, 3,4-heptadiene, 3,5-heptadiene, and cycloheptadiene. These diene-based monomers may be used solely or in combination of two or more.

[0030]

Examples of other monomers usable in combination with the diene-based monomers include aromatic monomers such as styrene,  $\alpha$ -methylstyrene, o-methylstyrene, p-methylstyrene, m-methylstyrene, and vinyl naphthalene; alkyl (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, and butyl (meth)acrylate; mono- or dicarboxylic acids such as (meth)acrylic acid, crotonic acid, maleic acid, and itaconic acid or anhydrides of dicarboxylic acids; vinyl cyan compounds such as (meth)acrylonitrile; unsaturated compounds such as vinyl chloride, vinylidene chloride, vinyl methyl ketone, vinyl acetate, (meth)acrylamide, and glycidyl (meth)acrylate. These other monomers may be used solely or in combination of two or more.

In the case of combined use of these other monomers, the amount of the diene-based monomer to be employed is preferably 0.5% by weight or more, more preferably 1% by weight or more, further preferably 5% by weight or more.

[0031]

The diene-based (co)polymer obtainable by polymerizing or copolymerizing the above diene-based monomer(s) and other monomer(s) usable in combination with the diene-based monomer(s) may be any (co)polymer including a random copolymer and a block copolymer. Examples of preferred (co)polymer include isoprene homopolymer, butadiene homopolymer, isoprene-styrene random copolymer, isoprene-styrene block copolymer, styrene-isoprene-styrene triblock copolymer, butadiene-styrene random copolymer, butadiene-styrene block copolymer, styrene-butadiene-styrene block copolymer, styrene-butadiene-styrene triblock copolymer, and ethylene-propylene-diene triblock copolymer. Examples of more preferred copolymer include isoprene-styrene block copolymer, styrene-isoprene-styrene triblock copolymer, butadiene-styrene block copolymer, styrene-butadiene-styrene block copolymer, and styrene-butadiene-styrene triblock copolymer.

[0032]

The diene-based sulfonyl group-containing (co)polymer to be used in the invention is prepared by sulfonating a (co)polymer in accordance with a known sulfonating method, for example, the method described in Shin-Jikken Koza (Vol. 14, III. p. 1773) edit. by the Chemical Society of Japan or Japanese Patent Laid-Open No. 227403/1990, the (co)polymer being obtainable by hydrogenating part or all of the remaining double bonds in the above diene-based (co)polymer and/or derived from the precursor monomer.

By the way, the above hydrogenation may be conducted after the sulfonation.

Examples of a sulfonating agent include sulfuric anhydride, sulfuric acid, chlorosulfonic acid, fuming sulfuric acid, and hydrogen sulfites (Li salt, Na salt, K salt, Rb salt, Cs salt, or the like).

The amount of the sulfonating agent is preferably from 0.005 to 1.5 mol, more preferably from 0.01 to 1.0 mol relative to 1 mol of the above (co)polymer.

[0033]

The diene-based sulfonyl group-containing (co)polymer of the invention is obtained by successively treating the product sulfonated as above with water and/or a basic compound. Examples of the basic compound include alkali metal hydroxides, alkali metal alkoxides,

alkali metal carbonates, ammonia water, organometallic compounds, and amines. The basic compound may be used solely or in combination of two or more. The amount of the basic compound to be used is 2 mol or less, preferably 1.3 mol or less relative to 1 mol of the sulfonating agent used.

[0034]

The diene-based sulfonyl group-containing (co)polymer thus obtained is preferably used as an emulsion in water. The emulsion is obtained by stirring and mixing the product after neutralization with water and/or a basic compound or before neutralization (a solution of the sulfonated product in an organic solvent) to emulsify the product, and then removing the organic solvent while the water being left.

The content of the diene-based sulfonyl group-containing (co)polymer is preferably from 0.1 to 20% by weight, more preferably from 0.2 to 10% by weight in an aqueous ink composition. When the content is less than 0.1% by weight, there exists a problem that a sufficient friction resistance cannot be attained in some cases, while when the content is more than 20% by weight, there arise problems that the viscosity of the ink composition may exceeds the viscosity most suitable for ink head and ejection stability is deteriorated.

[0035]

Examples of the monomer used for obtaining the non-diene-based sulfonyl group-containing (co)polymer include vinyl monomers such as allylsulfonic acid, vinylsulfonic acid, or methacrylsulfonic acid obtainable by reacting isobutylene and sulfur trioxide; styrene monomers such as sodium p-styrenesulfonate (e.g., Spiromer manufactured by Tosoh Corporation); or monomers having sulfonyl group such as a methacrylate ester monomer represented by the general formula:

$\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}(\text{AO})_n\text{SO}_3\text{Na}$  (A: a lower alkylene group)  
(e.g., Eleminol RS-30, manufactured by Sanyo Kasei K.K.);  
and sodium salts, potassium salts, and lithium salts of the above monomers.

[0036]

The non-diene-based sulfonyl group-containing (co)polymer can be copolymerized with a monomer containing no sulfonyl group. Examples of other copolymerizable monomer include aromatic monovinyl compounds such as styrene, ethylvinylbenzene,  $\alpha$ -methylstyrene, fluorostyrene, and vinylpyrene; acrylate ester monomers such as butyl acrylate, 2-ethylhexyl acrylate,  $\beta$ -methacryloyloxyethyl hydrogen phthalate, and N,N'-dimethylaminoethyl acrylate; methacrylate ester monomers such as 2-ethylhexyl methacrylate, methoxy

diethylene glycol methacrylate, methoxy polyethylene glycol methacrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, N,N'-dimethylaminoethyl methacrylate, and glycidyl methacrylate; cyanated vinyl compounds such as acrylonitrile and methacrylonitrile; silicon-modified monomers; and macromonomers.

Furthermore, there may be mentioned conjugated double bond compounds such as butadiene and isoprene; vinyl ester compounds such as vinyl acetate; and  $\alpha$ -olefin compounds such as 4-methyl-1-pentene. Among the copolymerizable monomers, preferred are styrene, methyl methacrylate, and acrylonitrile.

The amount of the copolymerizable monomer to be used is usually from 1 to 93% by weight, preferably from 5 to 80% by weight based on polymerizable monomers.

[0037]

The non-diene-based sulfonyl group-containing (co)polymer is obtained by radical polymerization of the above sulfonyl group-containing monomer or the sulfonyl group-containing monomer and other copolymerizable monomer in a solvent for polymerization such as water or an organic solvent using a radical polymerization initiator or a chain transfer agent.

Examples of the organic solvent for polymerization to be used for radical polymerization include alcohols



such as methanol, ethanol, and isopropanol; aromatic hydrocarbons such as xylene, toluene, and benzene; aliphatic hydrocarbons such as butane, pentane, hexane, cyclohexane, and heptane. Among the solvent for polymerization, preferred is water or methanol.

[0038]

Examples of the radical polymerization initiator include persulfate-type initiators such as potassium peroxide, sodium persulfate, and ammonium persulfate; inorganic initiators such as hydrogen peroxide; organic peroxides such as cumene hydroperoxide, isopropylbenzene hydroperoxide, p-menthane hydroperoxide, benzoyl peroxide; and organic initiators represented by azo-type initiators such as azobisisobutyronitrile.

[0039]

The non-diene-based sulfonyl group-containing (co)polymer obtainable by polymerizing or copolymerizing the above non-diene-based sulfonyl group-containing monomer(s) may be any (co)polymer including a random copolymer and a block copolymer.

[0040]

The non-diene-based sulfonyl group-containing (co)polymer to be used in the invention is preferably used as an emulsion in water. The emulsion is obtained by stirring and mixing the product after neutralization

with water and/or a basic compound or before neutralization (a solution of the sulfonated product in an organic solvent) to emulsify the product, and then removing the organic solvent while the water being left.

The content of the non-diene-based sulfonyl group-containing (co)polymer is preferably from 0.1 to 20% by weight, more preferably from 0.2 to 10% by weight in an aqueous ink composition. When the content is less than 0.1% by weight, there exists a problem that a sufficient friction resistance cannot be attained in some cases, while when the content is more than 20% by weight, there arise problems that the viscosity of the ink composition may exceeds the viscosity most suitable for ink head and ejection stability is deteriorated.

[0041]

As the ultra-penetrating agent to be contained in the aqueous ink composition of the invention, there may be mentioned acetylene glycols, acetylene alcohols, and glycol ethers.

They can be, of course, used in combination and, for example, it is also possible to use acetylene glycols and/or acetylene alcohols in combination with glycol ethers.

Specific examples of the acetylene glycols include acetylene glycol surfactants such as 2,4,7,9-tetramethyl-

5-decyn-4,7-diol and 3,6-dimethyl-4-octyn-3,6-diol, e.g., Surfynol 104 ( $m+n=10$  in the above formula 1), 82, 465, 485, or TG ( $m=n=0$  in the above formula 1) manufactured by Air Products and Chemicals Inc. In particular, a satisfactory record quality can be attained with the use of Surfynol 104 or TG.

Specific examples of the acetylene alcohols include 3,5-dimethyl-1-hexyn-3-ol and 2,4-dimethyl-5-hexyn-3-ol.

The content of the acetylene glycol and/or acetylene alcohol is preferably from 0.05 to 5% by weight, more preferably from 0.1 to 2% by weight in an aqueous ink composition. When the content is less than 0.05% by weight, there exists a problem that a sufficient penetrating ability cannot be attained in some cases, while when the content exceeds 5% by weight, there arises a problem that ejection stability is deteriorated owing to the incomplete dissolution in the ink composition.

[0042]

Examples of the glycol ethers include lower alkyl ethers of polyhydric glycols such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, and triethylene glycol monobutyl ether. In particular, a satisfactory record

quality can be attained with the use of triethylene glycol monobutyl ether.

The content of the glycol ether is preferably from 0.5 to 20% by weight, more preferably from 1 to 10% by weight in an aqueous ink composition. When the content is less than 0.5% by weight, there exists a problem that a sufficient penetrating ability cannot be attained in some cases, while when the content exceeds 20% by weight, there arise problems that the viscosity of the ink composition becomes very high and the stability of the aqueous ink composition decreases.

[0043]

The aqueous ink composition of the invention contains the following various components in an aqueous medium. The aqueous medium is water or a mixture of water and a water-soluble organic solvent.

The water-soluble organic solvent may include organic solvents having a low boiling point (particularly, alcohols having a low boiling point). Examples of the alcohols having a low boiling point include aliphatic alcohols having 1 to 4 carbon atoms such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol, and isobutyl alcohol. These organic solvents

having a low boiling point may be used solely or in combination of two or more.

The content of the organic solvents having a low boiling point (particularly, alcohols having a low boiling point) is preferably from 1 to 30% by weight, more preferably 10 to 20% by weight. When the content exceeds 30% by weight, a problem of ejecting property may arise, while when the content is less than 1% by weight, the rate of drying may decrease.

[0044]

The aqueous ink composition of the invention may contain other additives, for example, a pH regulator, an antiseptic agent, and/or an antifungal agent. Examples of the pH regulator include various amines such as diethanolamine and triethanolamine, and alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, and lithium hydroxide.

[0045]

Moreover, the aqueous ink composition of the invention has a surface tension at 20°C of preferably 20 to 45 dyn/cm, more preferably 25 to 40 dyn/cm.

Furthermore, the aqueous ink composition of the invention is preferably used as an ink for ink jet recording.

[0046]

The following will explain preparative examples of emulsions of the sulfonyl group-containing (co)polymers to be used at the preparation of the aqueous ink compositions of the invention, but the invention is, of course, not limited to the following preparative examples.

<Emulsion 1>

(1) Into a glass-made reaction vessel was placed 100 g of dioxane, and 11.8 g of sulfuric anhydride was added thereto while the inner temperature was maintained at 25°C. After 2 hours of stirring, a sulfuric anhydride-dioxane complex was obtained.

(2) Into a THF solution (concentration = 15%) of 100 g of styrene/isoprene/styrene triblock copolymer (ratio by weight = 10/80/10, Mw = 100000) was added all the amount of the complex obtained in (1) while the inner temperature was maintained at 25°C. The stirring was continued for further 2 hours.

(3) Into a flask were placed 1200 g of water, 7.1 g of sodium hydroxide, and 1 g of sodium dodecylbenzenesulfonate, and the inner temperature was maintained at 40°C. All the amount of the solution obtained in (2) was added dropwise thereinto over a period of 1 hour while the inner temperature was maintained at 40°C. After the addition, the whole was stirred at 40°C for 2 hours and the solvent was removed by

distillation under reduced pressure while the water was left to obtain a sulfonated polymer emulsion having a concentration of 15%. The particle diameter of the polymer was 30 nm and the content of sulfonic acid in the solid mass was 1.2 mmol/g.

[0047]

<Emulsion 2>

(1) Into a glass-made reaction vessel was placed 100 g of 1,2-dichloroethane, and 11.8 g of sulfuric anhydride was added thereto while the inner temperature was maintained at 25°C, whereby a 1,2-dichloroethane solution of sulfuric anhydride was obtained.

(2) Into a 1,2-dichloroethane solution (concentration = 15%) of 100 g of hydrogenation product (hydrogenation rate 99%) of the diene units of butadiene/styrene/butadiene copolymer (ratio by weight = 30/40/30, Mw = 50000) was added all the amount of the sulfuric anhydride solution obtained in above (1) over a period of 1 hour while the inner temperature was maintained at 25°C. The stirring was continued for further 2 hours. After stirring, about 500 g of 1,2-dichloroethane was removed under reduced pressure and then 500 g of THF was added thereto.

(3) Into a flask were placed 1200 g of water, 7.1 g of sodium hydroxide, and 1 g of sodium

dodecylbenzenesulfonate, and the inner temperature was maintained at 40°C. All the amount of the solution obtained in (2) was added dropwise therein over a period of 1 hour while the inner temperature was maintained at 40°C. After the addition, the whole was stirred at 40°C for 2 hours and the solvent was removed by distillation under reduced pressure while the water was left to obtain a sulfonated polymer emulsion having a concentration of 15%. The particle diameter of the polymer was 40 nm and the content of sulfonic acid in the solid mass was 1.0 mmol/g.

[0048]

#### <Emulsion 3>

To a 500 ml round-bottomed four-necked flask were added 0.75 g of Emal O (an alkyl sulfate-type anionic emulsifying agent) and 155 g of distilled water. After replacement by nitrogen gas under slow stirring, 20 g of a mixed monomer composed of 40 g of vinylsulfonic acid and 40 g of methacrylic acid was added thereto. The bath temperature was maintained at 30°C, and after about 20 minutes, one tenth of 10 ml of an aqueous solution containing 0.75 g of potassium persulfate and 10 ml of an aqueous solution containing 0.75 g of acid sodium bisulfite. After 30 minutes, 60 g of the remaining mixed monomer was added dropwise over a period of 3 hours and



the polymerization initiators were also added portionwise before the completion of the addition of the monomer. After the addition, the stirring was continued for 1 hour, and the mixture was salted out by 1/2 mol of aqueous sodium sulfate solution, washed, and then dried.

The resulting copolymer was dissolved in toluene. Thereafter, the toluene solution was stirred and mixed with water to emulsify the copolymer and the toluene was removed while the water was left, whereby Emulsion 3 was obtained.

[0049]

#### [Examples]

The following will explain the invention specifically with reference to Examples and Comparative Examples, but the invention is not limited to the following Examples.

[0050]

#### [Example 1]

##### Ink Set A

##### (Pigment Dispersion A)

Pigment Yellow 128	25% by weight
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Styrene-acrylic acid copolymer

(a dispersant resin)	5% by weight
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Pigment Yellow 128 and the dispersant resin were mixed and the concentration of the dispersed pigment is

regulated to be 25% by adding pure water to obtain a mixture. The mixture was dispersed together with glass beads (diameter: 1.7 mm, an amount of 1.5 times (by weight) of the mixture) for 2 hours in a sand mill manufactured by Yasukawa Seisakusyo K.K. After the dispersing, glass beads were removed and then the following components were added thereto. After stirring at ambient temperature for 20 minutes, the mixture was filtrated through an 8 $\mu$ m membrane filter to obtain Pigment Dispersion A.

[0051]

• Yellow Ink Composition A

Pigment Dispersion A	12.5% by weight
Emulsion 1	6.7% by weight
Glycerin	10% by weight
Surfynol 104	1% by weight
Triethylene glycol	
monobutyl ether	5% by weight
Pure water	remainder

[0052]

• Magenta Ink Composition A

Magenta Ink Composition A was obtained in a similar manner to the preparation of Yellow Ink Composition A with the exception that Pigment Red 122 was employed as the pigment instead of Pigment Yellow 128.

[0053]

• Cyan Ink Composition A

Cyan Ink Composition A was obtained in a similar manner to the preparation of Yellow Ink Composition A with the exception that Pigment Blue 15:3 was employed as the pigment instead of Pigment Yellow 128.

[0054]

[Example 2]

Ink Set B

Ink Set B (Yellow Ink Composition B, Magenta Ink Composition B, and Cyan Ink Composition B) was obtained in a similar manner to the preparation of Ink Set A with the exception that Emulsion 2 was employed instead of Emulsion 1 and Surfynol TG was employed instead of Surfynol 104.

[0055]

[Example 3]

Ink Set C

Ink Set C (Yellow Ink Composition C, Magenta Ink Composition C, and Cyan Ink Composition C) was obtained in a similar manner to the preparation of Ink Set A with the exception that Emulsion 3 was employed instead of Emulsion 1.

[0056]

[Comparative Example 1]

#### Ink Set D

Ink Set D (Yellow Ink Composition D, Magenta Ink Composition D, and Cyan Ink Composition D) was obtained in a similar manner to the preparation of Ink Set A with the exception that Emulsion 1 was not added.

[0057]

The following evaluation tests were conducted on each aqueous ink composition obtained in Examples and Comparative Example. Results are shown in Table 1.

#### <Evaluation of cohesion differential>

The aqueous ink compositions of above Ink Set A to D were loaded on an ink jet recording apparatus MC-2000 manufactured by Seiko Epson Corporation, and printing was conducted with the combination of yellow and magenta or yellow and cyan at the same print duty in regard to each ink composition on MC photographic paper manufactured by Seiko Epson Corporation. The resulting prints were evaluated in accordance with the following judging standard.

Judgment A: No cohesion differential occurs even when total of print duty of each ink composition is 140%.

Judgment B: Cohesion differential occurs when total of print duty of each ink composition is 120% or more.

Judgment C: Cohesion differential occurs when total of print duty of each ink composition is 100% or more.

[0058]

<Evaluation of gloss differential>

Magenta ink compositions A to D were loaded on an ink jet recording apparatus MC-2000, and a color patch was printed on MC photographic paper at a print duty of 10%, 20%, 40%, 60%, 80%, or 100%. The samples were observed visually from various angles and evaluated in accordance with the following judging standard.

Judgment A: The difference of gloss is hardly noticeable even between different print duties.

Judgment B: The difference of gloss is observed but is not so remarkable between different print duties.

Judgment C: The difference of gloss is noticeable between different print duties.

[0059]

<Evaluation of bronzing>

Cyan ink compositions A to D were loaded on an ink jet recording apparatus MC-2000, and a color patch was printed on MC photographic paper at a print duty of 10%, 20%, 40%, 60%, 80%, or 100%. The samples were observed visually from various angles and evaluated in accordance with the following judging standard.

Judgment A: Reddish coloring is not observed or is hardly noticeable at all the print duties.

Judgment B: Reddish coloring is observed at one or two print duties.

Judgment C: Reddish coloring is observed at three or more print duties.

[0060]

<Evaluation of fixing ability>

Aqueous ink compositions of Ink Sets A to D were loaded on an ink jet recording apparatus MC-2000, and printing was conducted on MC glossy paper. The printed part was strongly rubbed with a finger at 30 minutes after the printing, and evaluation was conducted in accordance with the following judging standard.

Judgment A: No staining occurs.

Judgment B: Staining slightly occurs

Judgment C: Staining occurs.

[0061]

<Evaluation of ejection stability>

Aqueous ink compositions of Ink Sets A to D were loaded on an ink jet recording apparatus MC-2000, and 500 sheets of a pattern comprising text and graphics as A4 size were printed. Cleaning was conducted at the time when any missing or bend occurred, and evaluation was conducted based on the number of cleaning times required during 500 sheets of printing in accordance with the following judging standard.

Judgment A: The number of cleaning times is 1 time or less.

Judgment B: The number of cleaning times is from 2 to 4 times.

Judgment C: The number of cleaning times is 5 times or more.

[0062]

[Table 1]

	Ink Set A	Ink Set B	Ink Set C	Ink Set D
	Example 1	Example 2	Example 3	Comparative Example 1
Cohesion differential	A	A	A	B
Gloss differential	A	A	A	C
Bronzing	A	A	A	B
Fixing ability	A	A	A	C
Ejection stability	A	A	A	A

[0063]

[Advantage of the Invention]

As detailed above, the invention provides a pigment-containing aqueous ink composition excellent in light-fastness and water-fastness wherein a dispersing polymer, a sulfonyl group-containing (co)polymer and an ultra-penetrating agent are contained, whereby there are exhibited excellent effects that cohesion differential, color-floating phenomenon, color-bleeding, and the like are not occurred, and improved fixing ability and coloring property are realized without impairing ejection stability.